



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification: C09C 1/42, C09D 5/00, D21H 17/68, D21H 17/69, D21H 19/40	A1	(11) International Publication Number: WO 00/32700 (43) International Publication Date: 08 June 2000 (08.06.2000)
(21) International Application Number: PCT/US99/28235 (22) International Filing Date: 30 November 1999 (30.11.1999) (30) Priority Data: 09/204,610 02 December 1998 (02.12.1998) US (60) Parent Application or Grant ENGELHARD CORPORATION [/]; (). JENSEN, Amy, S. [/]; (). MATHUR, Sharad [/]; (). RIGGS, Kevin, C. [/]; (). BURBANK, Tracey, A. [/]; (). LONDO, Michael, G. [/]; (). MILLER, Stephen, I. ; ().		Published
(54) Title: HIGH OPACITY KAOLIN HYBRID PIGMENTS (54) Titre: PIGMENTS HYBRIDES DE KAOLIN A OPACITE ELEVEE (57) Abstract <p>A composition and a method is disclosed relating to novel clay pigments comprised of a metal oxide and/or metal oxide precursor (metal oxides and metal oxide precursors of transition metals, post-transition metals, or their mixtures) which are thermally aggregated with hydrous clay. The method involves heating a mixture of the clay and metal oxide, metal oxide precursor and/or combinations thereof to the extent necessary to aggregate the metal oxide and/or metal oxide precursor with the clay. The pigments of this invention provide a new pigment having opacity useful in paper coating and filling applications.</p> (57) Abrégé <p>L'invention concerne une composition et un procédé relatifs à de nouveaux pigments d'argile comprenant un oxyde métallique et/ou un précurseur d'oxyde métallique (oxydes métalliques et précurseurs d'oxydes métalliques de métaux de transition, de métaux de post-transition, ou leurs mélanges) qui sont agrégés thermiquement à de l'argile hydratée. Le procédé consiste à chauffer un mélange argile/oxyde métallique, précurseur d'oxyde métallique et/ou combinaisons de ces derniers à une température nécessaire pour agréger l'oxyde métallique et/ou le précurseur d'oxyde métallique à l'argile. Les pigments selon l'invention permettent de produire un nouveau pigment dont l'opacité convient pour des applications de couchage et de charge du papier.</p>		

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(21) International Application Number: PCT/US99/28235 (22) International Filing Date: 30 November 1999 (30.11.99) (30) Priority Data: 09/204,610 2 December 1998 (02.12.98) US (71) Applicant: ENGELHARD CORPORATION [US/US]; 101 Wood Avenue, P.O. Box 770, Iselin, NJ 08830-0770 (US). (72) Inventors: JENSEN, Amy, S.; 194 Tennis Court, Wall Township, NJ 07719 (US). MATHUR, Sharad; Apartment 2201, 1900 Wesleyan Drive, Macon, GA 31210 (US). RIGGS, Kevin, C.; 718 Wedgewood Court, Macon, GA 31211 (US). BURBANK, Tracey, A.; 1754 South Pine Circle, Macon, GA 31211 (US). LONDO, Michael, G.; 743 Horseshoe Bend Drive, Macon, GA 31211 (US). (74) Agents: MILLER, Stephen, I. et al.; Engelhard Corporation, 101 Wood Avenue, P.O. Box 770, Iselin, NJ 08830-0770 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: HIGH OPACITY KAOLIN HYBRID PIGMENTS (57) Abstract A composition and a method is disclosed relating to novel clay pigments comprised of a metal oxide and/or metal oxide precursor (metal oxides and metal oxide precursors of transition metals, post-transition metals, or their mixtures) which are thermally aggregated with hydrous clay. The method involves heating a mixture of the clay and metal oxide, metal oxide precursor and/or combinations thereof to the extent necessary to aggregate the metal oxide and/or metal oxide precursor with the clay. The pigments of this invention provide a new pigment having opacity useful in paper coating and filling applications.		

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Description

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HIGH OPACITY KAOLIN HYBRID PIGMENTS

BACKGROUND OF THE INVENTION

1.1 Field of the Invention

This invention relates to novel mineral-based pigments for providing opacity and brightness to paper. More particularly, the present invention relates to the thermal aggregation of hydrous clay particles with metal oxides and/or metal oxide precursors.

1.2 Related Art

Much research has been and continues to be devoted to providing low cost opacifying pigments as substitutes for more expensive opacifying pigments such as titania.

One approach consists of "bulking" hydrous clays into larger aggregates. In this approach smaller clay particles are either chemically or thermally bonded to larger clay particles to form a larger, bulkier particle. The larger particle size is beneficial in improving the pigments light scattering ability, which is a key property in order to have a high opacity pigment. U.S. Patent No. 4,738,726 is one example of the bulking approach using cationic polymers to aid in particle aggregation of hydrous clays.

Another approach is to perform controlled calcination of the clay. U.S. Patent No. 3,586,523 describes calcined hard clays of improved opacity.

The present invention offers an advance from known techniques and compositions of clay-based opacifying pigments as hereinafter described.

SUMMARY OF THE INVENTION

The present invention relates to a composition and method of making compositions of hybrid opacifying pigments useful as paper filling or paper coating pigments. The composition comprises a pigment derived from heating a hydrous clay with metal oxides and/or metal oxide precursors, the metal being selected from the group consisting of a transition metals, post-transition metals, and their combinations,

the heating being applied to an extent sufficient to change the crystalline structure of the clay while aggregating or structuring the clay with the metal oxides, their precursors, and/or combinations thereof.

Advantages of the hybrid pigments of the present invention include pigments of significantly higher opacity when compared to a simple physically combined blend (i.e., not heated) of commercially available calcined kaolin pigments and the corresponding metal oxide and/or metal oxide precursor. A further surprising and quite unexpected advantage of this invention includes that when the hybrid pigments are used in sheet paper applications, they impart equal or comparable sheet brightness and significantly greater opacity at equivalent net mineral content than commercially available calcined kaolin pigments. That is to say despite the fact the hybrid pigments of the invention may have lower GE Brightness (GEB) values than some of the best commercially available calcined clay opacifying pigments, the hybrid pigments of this invention provide comparable coated sheet brightness but surprisingly superior sheet opacity at equivalent net mineral contents compared to these commercially available pigments.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The Hydrous Clay

As used herein, the term "hydrous clay" is intended to describe a clay which has not been subjected to calcination, i.e., a temperature at which the basic crystalline structure of the clay would be altered. In the case of kaolin, maintaining the clay at temperatures under 450°C will not alter the kaolin's crystalline structure.

Hydrous clays are widely known in the art and are typically produced from crude clays which have been subjected to beneficiation, as for example to, froth flotation, magnetic separation, mechanical delamination, grinding, or similar commutation.

Examples of hydrous clays are kaolinite, halloysite, montmorillonoids (e.g.,

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10 talc, pyrophyllite, hectorite, bentonite and montmorillonite), smectites, attapulgite, illite, and sepiolite. Characteristic of these hydrous clay is that they contain chemically bound water (i.e., water of hydration) which is driven off by heating.

5 A preferred hydrous clay is derived from kaolinite. Kaolinite is an aluminum hydroxide silicate having the approximate composition of $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$.

15 It is known that the shape of the particle size distribution curve of the hydrous clay has an effect on the pigment's end-use application such as in coating. A clay having the following particle size distribution characteristics has been found to provide excellent rheology: a median particle size of 0.55 micrometers and a particle
20 size distribution such that about 88 +/- 2% of the particles have an equivalent spherical diameter less than about 2 micrometers and not more than about 25% by weight, preferably not more than about 20% by weight, have an equivalent spherical diameter less than 0.3 micrometers. If the quantity of ultrafine particles, i.e., particles
25 0.3 micrometers and finer, is too great, the rheology of the pigment may be such that
15 it has limited, if any, use.

30 In order to achieve the desired particle size distribution of the hydrous clay, it is generally necessary to perform one or more particle size separations on the crude clay. Generally, such processing includes degritting, followed by differential gravitational or centrifugal sedimentation to recover a size fraction of desired particle
35 size, such as for example, a fraction that is 90% by weight finer than 1 micrometers and does not contain an excessive amount of ultrafine particles. The content of ultrafines and median (weight) particle size of such fraction will vary, depending on the particle size distribution of the crude clay. In order to perform these operations
40 successfully, it is essential that the clay be present in the form of discrete particles in
25 water rather than flocs so that the particles can be accurately separated into different size ranges. The clay particles are therefore treated with a deflocculant (dispersing agent) which will give all the particles a negative electric charge, and cause them to repel each other when the particles are suspended in water. The clay dispersant used
45 at this stage is generally referred to as a "primary" dispersant. Dispersants used to
30 deflocculate suspensions of previously processed clay (such as dispersants added to
50 filter cakes) are termed "secondary" dispersants or deflocculants. Suitable dispersing

agents used for primary dispersion in practice of the present invention are conventional and include water soluble salts of a condensed phosphate, e.g., sodium hexametaphosphate or tetrasodium pyrophosphate, a water soluble salt of a polysilicic acid, for example, sodium silicate, or a water soluble organic polymeric dispersing agent, for example a polyacrylate or a polymethylmethacrylate salt having a molecular weight in the range of about 500 to about 10,000. The amount of dispersing agent used will generally be in the range of from about 0.025 to 0.2% by weight based on the weight of the dry clay. Generally, particle size separations are performed using deflocculated aqueous suspensions having a solids content of about 20-60% by weight.

Other solids levels may be used to carry out such separations. The median particle size of the clay particles should range from 0.4 to 0.7 micrometers, equivalent spherical diameter (e.s.d.), preferably 0.5 to 0.6 micrometers, as determined by conventional sedimentation techniques using the SEDIGRAPH® particle size analyzer, supplied by Micromeritics, Inc. From about 75% to 95% by weight of the particles should be finer than 2 micrometers, e.s.d. The content of fines below 0.3 micrometer e.s.d. should be below 35 weight percent, preferably below 25 weight percent, and most preferably 20 weight percent or below. It should be understood that the measurements of the size of clay particles that are 0.3 micrometer or finer are of limited reproducibility. Thus, when a SEDIGRAPH® analyzer is employed, the value for weight percent may be +/- 5% when tested by another operator or a different SEDIGRAPH® analyzer is employed. Most preferably, median particle size is 0.6 +/- 0.05 micrometers, e.s.d., with 85 to 95% by weight of the particles finer than 2 micrometers, e.s.d., and less than about 20% by weight or less finer than 0.30 micrometers, e.s.d. Blending of clay fractions may be advantageous or necessary with some crudes to provide a clay feed having a desirable particle size distribution. Also useful are hydrous clays derived from fine grained East Georgia crudes; e.g., a hydrous clay product with approximately 90 percent of the particles finer than 0.5 micrometer.

Illustrative of particle size distributions for beneficiated hydrous clays useful in this invention excellent results have been obtained using hydrous clays ranging from about 75 to 100 percent by weight finer than 1 micrometer with approximately

5 70-90 percent of the particles finer than 0.5 micrometer. A particularly useful
hydrous clay characteristic of the hydrous clays used in the examples of this
10 application has a particle size distribution of about 85 to 95 percent by weight finer
than 1 micrometer with approximately 70 to 80 percent by weight of the particles finer
5 than 0.5 micrometer.

15 The Metal Oxides and Their Precursors

The metal oxides and metal oxide precursors useful in this invention are
derived from transition metals, post-transition metals, and their combinations.

20 10 The term "precursor" as used herein when referring to metal oxide precursors
is intended to describe a metal composition that when sufficiently heated will form the
metal composition's corresponding metal oxide. In the case of titania (titanium
dioxide), the corresponding titania precursor may be a metal composition in the form
25 of titanyl sulfate, titanyl chloride, or other appropriate forms. Typical heating
15 temperature wherein an oxide will be formed from its precursor can readily be
determined by one skilled in the art by thermogravimetric analysis. In the case of
30 titanyl sulfate, titania will be formed at approximately 800 C.

Transition metals are metals having atomic numbers of 21 to 29 (scandium
through copper), 39 to 47 (yttrium through silver), 57 to 79 (lanthanum through gold),
35 20 and 89 and higher (actinium and higher). A preferred transition metal is titanium
which forms its corresponding metal oxide in the form of titania.

Post-transition metals are metals having atomic numbers of 30 to 32 (zinc
through germanium), 48 to 51 (cadmium through antimony), and 80 to 84 (mercury
40 through polonium). Preferred post-transition metals are zinc and tin which form the
25 corresponding metal oxides of zinc oxide for zinc and stannous oxide (SnO) and/or
stannic oxide (SnO₂) for tin.

The metal oxides and their precursors will typically be in the form of powders
45 having particle sizes in the range of less than 5 μm , and in the case of titania particle
sizes of 1 μm , typically between 0.3 to 0.6 μm .

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The Inventive Composition

An essential feature of the invention is that the transition or post-transition metals oxides and/or their precursors be added to the hydrous clay prior to heat treatment. The presence of the metal oxides and/or their precursors during the formation of the highly reactive phases (e.g., metakaolin and fully calcined temperature ranges) the clay undergoes crystalline restructuring and promotes the metal oxides and/or their precursors aggregation with the clay.

As noted above, heating is applied to the extent necessary to alter the crystalline structure of the clay and cause the metal oxide to aggregate with the altered clay. Of course in the case of when a metal oxide precursor is used, heating needs to also be sufficient to form the corresponding metal oxide along with aggregation with the altered clay.

Preferably, heating of the metal oxide or its precursor with a hydrous clay is carried out at temperatures not higher than about 1200°C when the clay is kaolinite. Above this temperature, the resulting pigment may be too abrasive for application as a filling or coating pigment. Thus, the upper temperature limit of the heating may vary somewhat according to the acceptable abrasiveness of the pigment's application and based on the type of hydrous clay being used.

In the case of kaolinite as the hydrous clay, heating with the metal oxide is preferably in the range of 400 to 1100°C.

The precise degree of heating will depend on a number of considerations that should be apparent to one of ordinary skill in the art. For example, if the application for a kaolin pigment requires low abrasion as in newsprint, lower heating temperatures in the range of 400 to 800°C (i.e., covering temperature range not exceeding metakaolin temperature of 760°C by too much) will result in a lower abrasive pigment than if the foregoing temperature range is exceeded. If coarser pigments are required, for example, to help improve pigment retention within the fiber web of paper, heating above the foregoing temperature range near or around the fully calcined temperature of 1200°C.

The amount of metal oxide and/or its precursor used in accordance with this invention may widely vary. From an economic standpoint, it is desirable to use a minor

5 amount of the metal oxide and/or its precursor with respect to the hydrous clay, i.e., less
than 50 weight percent based on the total dry weight of the clay and metal oxide and/or
10 precursor, e.g., from 0.5 to 50 weight percent. As shown in the following examples,
excellent results have been achieved in amounts ranging from 5 to 20, more preferably
5 from 8 to 12 weight percent of metal oxide and/or precursor. As alluded to above,
improved results will likely be achieved at majority amounts of metal oxide and/or
15 precursors. However, these will be a less economically viable embodiments as the
invention will contain a higher fraction of the more costly metal oxide/precursor.

Pigments of this invention may be prepared by wet blending or dry blending of
20 the hydrous clay (spray-dried hydrous clay if dry blending) and metal oxide and/or its
precursor prior to heating.

Dry blending may be accomplished in any type of conventional mixing devices
25 such as a V-blender, paddle mixer, helical screw or roller mill.

Wet blending of the invention's constituents may be done in any of a number of
15 wet blending devices such as impeller mixers, sigma mixers, double planetary mixers,
or drill presses with an up-lift blade. After sufficient mixing, the mixture of constituents,
30 may be screened through a mesh screen and spray dried.

In either the dry or wet blending techniques as discussed above, the resulting
mixtures may be pulverized before the heating step to break up agglomerates to form
20 discrete particles. Typical milling is done until the particle size of the mixture is
35 approximately 90 percent less than 1 μm .

The pigments of this invention are minerals which find uses as paper fillers and
in paper coatings which are essential components of many paper grades and represent the
40 largest non-fibrous component of paper. These minerals are utilized by papermakers to
25 enhance certain printing and writing characteristics, such as paper brightness, opacity,
gloss, smoothness and ink absorption. Filler addition levels usually range from 3 percent
to 30 percent of the total weight of paper. Typical mineral fillers used in papermaking
45 include TiO_2 (rutile and anatase forms), kaolin clay, talc, calcium carbonate, aluminum
trihydrate, synthetic silicas and plastic pigments. Crystalline filler minerals are used in
30 concert with several wet end papermaking additives: retention/drainage aids
50 (polyacrylamides, polyamines, polydadmecs and polyethyleneimines), wet strength

additives (urea-formaldehydes, melamine formaldehydes or polyamine epichlorohydrins), dry strength additives (starches, gums), sizing agents (ASA, AKD and alum-rosin) and fluorescent paper dyes.

When the finished application of the paper calls for printing on both the front and back sides of an uncoated sheet, as in the case of newspapers, magazines and books, the most common reason for adding fillers to the paper furnish is to improve opacity. A sheet low in opacity, allows the printed material on the reverse side to show through, thereby making the page difficult to read. A highly filled sheet contains discrete mineral particles that serve as scattering centers, which scatter light back to the viewers eye, rather than allowing it to be transmitted through the sheet to illuminate the print on the reverse side.

The ability to effectively scatter light is related to the refractive index of the mineral filler. A higher refractive index serves to decrease the velocity of light as it passes through the material and increases the angle at which the light ray is bent upon entering the media. The rutile form of TiO_2 has the highest refractive index, and is the most expensive, of the common paper filler minerals. Calcined kaolin clay is a cheaper alternative, but is also a distant second in terms of refractive index. Accordingly, calcined kaolin is used to "extend" TiO_2 , in order to reduce the cost of the papermaking process, while not tremendously sacrificing opacity. The large difference between the refractive indices, and hence the light scattering efficiency of calcined kaolin and rutile TiO_2 , naturally creates a gap which a hybrid pigment of this invention fills. The hybrid pigment of the invention is fully compatible with all of the common wet end papermaking additives.

Minerals as components in a paper or paperboard coating formulation are used to improve printability and appearance. In the most basic form, a paper coating consists of a pigment plus an adhesive used to bind the particles to one another as well as to the paper or paperboard basestock. Pigment coatings on paper promote improved smoothness, as well as controlled porosity, brightness and gloss, while pigment coatings on paperboard are used primarily for coverage of the unbleached baseboard. In this application, improved opacity is the primary function of the coating and a hybrid pigment of the invention would have application.

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In creating a coating color, the hybrid pigments of the invention are combined with an adhesive (casein, starches, polyvinyl alcohol, styrene-butadiene latex, etc.), a rheology modifier (either a secondary dispersant, such as a polyacrylate, or a thickener, such as carboxymethylcellulose), a microbial inhibitor (isothiazoline) and a pH modifier (ammonium hydroxide or caustic). Coating formulations containing hybrid pigments of the invention can be applied to paper and paperboard basestocks using any conventional technology.

Hybrid pigments of the invention have additional application as opacifiers in paint formulations as well.

EXAMPLES

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The following examples are intended to be illustrative of the invention and not limiting of the invention's full scope. As reported in the following examples, the following methods were used to determine values for the reported pigment properties: GE Brightness (GEB) by TAPPI 646 om-94; particle size distribution TAPPI 649 cm-90 using a SEDIGRAPH® analyzer, model #5100; and scatter coefficients were determined by coating kaolin clay suspensions onto black glass plates at a coat weight of 7.0-14.0 g/m² (expressed as dry clay). The reflectance of the coatings after drying in air at wavelengths of 457 nm and 577 nm (as reported) are measured by means of an Elrepho reflectometer. The reflectance values are converted by the use of Kubelka-Munk equations to light scattering values (m²/g). The light scattering values are a measure of the opacity potential of the clay because the higher values indicate that light rather than passing through is reflected and scattered back. The higher the light scattering value, the higher the opacity potential of the clay.

Example 1

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This example illustrates the improved properties and that the hybrid pigment of this invention possess including a comparative example against a simple mixture (i.e., non-heated) of the hybrid pigment's starting components.

A hydrous clay was heated to a temperature of approximately 930 C (1700°F) (metakaolin range) to form clay pigment, C-1, having the characteristics as reported in Table 1A. A hybrid pigment, H-1, characteristic of the present invention, was made by co-heating to a temperature of 930 C a mixture of 90 percent by weight of the hydrous clay used to make C-1 and 10 percent by weight of TiO₂ commercially available from DuPont Corporation under the tradename of RPS VANTAGE. The properties of H-1 are reported in Table 1A. In each case prior to heat treatment, C-1 and H-1 were pulverized by conducting 3 passes of each material through a Micro Mill brand pulverizer.

TABLE 1A

Property	C-1	H-1
Heat Treatment	930 C	930 C
Components (wt.%): Clay	100%	90%
TiO ₂	--	10%
Components Mixed Before Heat Treatment	Single Component N/A	YES
Components Mixed After Heat Treatment	Single Component N/A	NO
GEB	79.7	82.6
Scatter coefficient 457 nm(m ² /g)	0.268	0.381
Scatter coefficient 577 nm(m ² /g)	0.209	0.338
Particle Size (% < 2 μ)	86.7	88.7

Referring to Table 1A, one sees an increase in GEB value and significant increases in the scatter coefficients for the inventive pigment H-1 versus C-1 the hydrous clay pigment calcined to the metakaolin temperature range of approximately 930 C.

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Further comparative examples were prepared to compare the pigments of this invention with a clay calcined at 1090 C (2000°F) (fully calcined range) and with this fully calcined clay mixed with the equivalent amount of TiO₂ used in the inventive composition.

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5 The hydrous clay used to prepare pigment C-1, was again used to prepare pigment C-2 which differed from C-1 in being heated to a temperature of 1090 C (fully calcined range). Prior to heat treatment, the C-2 pigment was pulverized in the Micro Mill pulverizer (3 passes). Another sample containing 90 percent by weight of the hydrous clay used to make C-1 and 10 percent by weight RPS VANTANGE TiO₂,
10 were wet mixed prior to spray drying. The resulting mixture was pulverized in the Micro Mill pulverizer (3 passes) and then heated to 1090 C to form inventive pigment, H-2. A physical dry blend was prepared of 90 percent by weight C-2 and 10 percent by weight RPS VANTANGE TiO₂ by conducting 3 passes through the Micro Mill
25 pulverizer to form comparative pigment, C-3. The measured properties of C-2, C-3, and H-2 are reported in Table 1B.

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TABLE 1B

Property	C-2	C-3	H-2
Heat Treatment	1090 C	1090 C	1090 C
Components (wt.%): Clay TiO ₂	100% 10%	90% 10%	90% 10%
Components Mixed Before Heat Treatment	Single Component N/A	NO	YES
Components Mixed After Heat Treatment	Single Component N/A	YES	NO
GEB	92.7	93.1	81.5
Scatter Coefficient, 457nm (m ² /g)	0.296	0.314	0.368
Scatter Coefficient, 577nm (m ² /g)	0.256	0.269	0.328
Particle Size (% < 2 μ)	89.1	89.2	87.4

Referring to TABLE 1B, one sees that while the inventive composition, H-2, suffered from a lower GEB value versus comparative pigments C-2 and C-3, H-2 provided significantly higher scatter coefficients compared to C-2 and C-3. However, despite the lower GEB value for H-2, H-2 performed quite unexpectedly in coating formulations as reported in Example 4, wherein it is demonstrated that the lower GEB value for pigments of this invention did not have a negative effect on coated sheet brightness.

Example 2

This example exhibits the benefits of this invention are also obtainable by using a metal oxide precursor in the form of titanyl sulfate purchased from Kemira Pigments, Inc., of Savannah, GA, and available under the trade name UNITI 909. In this example, C-1 of Example 1 is also used for comparative purposes. Pigment C-4 was a physical dry blend of 90 percent by weight C-1 and 10 percent by weight UNITI 909 having been

pulverized by 3 passes through the Micro Mill pulverizer. Inventive pigment, H-3, was comprised of 90 percent by weight of the hydrous clay used to make C-1 and 10 percent by weight UNITI 909 having been wet mixed prior to spray drying H-3 was then pulverized (3 passes through the Micro Mill pulverizer) and heated to a temperature of 930 C. The properties of C-1, C-4, and H-3 are reported in TABLE 2.

TABLE 2

Property	C-1	C-4	H-3
Heat Treatment	930 C	930 C	930 C
Components (wt.%): Clay	100%	90%	90%
TiO ₂	—	10%	10%
Components Mixed Before Heat Treatment	Single Component N/A	NO	YES
Components Mixed After Heat Treatment	Single Component N/A	YES	NO
GEB	79.7	82.7	87.8
Scatter Coefficient, 457nm (m ² /g)	0.268	0.298	0.390
Scatter Coefficient, 577nm (m ² /g)	0.209	0.253	0.333
Particle Size (% < 2 μ)	86.7	91.6	90.9

Referring to TABLE 2, one sees excellent GEB values and scatter coefficients of inventive pigment H-3 compared to pigments C-1 and C-4. Thus, the benefits of heat treatment after mixing the components compared to a mere blend of components is clearly evident by the superior brightness and scatter coefficients of inventive pigment H-3.

Example 3

This example exhibits the effect of TiO_2 purity on the properties of the hybrid pigments of this invention. The compositions of the TiO_2 pigments tested are as follows:

	Al_2O_3	SiO_2	K_2O	Na_2O	Fe_2O_3	TiO_2	CaO	MgO	P_2O_5
TiO_2 - A ¹	0.5	ND ³	0.21	0.00	0.01	98.03	0.01	0.00	0.26
TiO_2 - B ²	0.0	ND ³	0.15	0.00	0.00	98.64	0.00	0.00	0.23

- Notes: 1 - TiO_2 used in Example 1 obtained from Dupont Chemical Company and available under trade name of RPS VANTANGE.
2 - TiO_2 obtained from Kronos Inc., of Houston, Texas and available under trade name KRONOS 1000.
3 - Not Detectable.
4 - All values in terms of mass %.

Additional comparative pigments were prepared for heat treatment at temperatures of 930 C and 1090 C. Thus, inventive pigment H-4 was made by heating to 930 C a mixture of 90 percent by weight of the same hydrous clay as used to make pigments C-1 and H-1 with 10 percent by weight of the purer KRONOS TiO_2 . Inventive pigment H-5 was made by heating to 1090 C a mixture of 90 percent by weight of the same hydrous clay as used to make pigments C-2 and H-2 with 10 percent by weight of the purer KRONOS TiO_2 . In both cases, H-4 and H-5 were pulverized in the Micro Mill pulverizer (3 passes) prior to heat treatment. Results for pigment property comparisons at 930 C and 1090 C are provided in TABLE 3A and TABLE 3B, respectively.

TABLE 3A

Property	C-1	H-1	H-4
Heat Treatment	930 C	930 C	930 C
Components (wt.%): Clay	100%	90%	90%
TiO ₂	--	10% ¹	10% ²
Components Mixed before Heat Treatment	Single Component N/A	YES	YES
Components Mixed After Heat Treatment	Single Component N/A	NO	NO
GEB	79.7	82.6	85.2
Scatter Coefficient, 457nm (m ² /g)	0.268	0.381	0.392
Scatter Coefficient, 577nm (m ² /g)	0.209	0.338	0.297
Particle Size (% < 2 μ)	86.7	88.7	93.0

Notes: 1 - RPS VANTANGE TiO₂, DuPont Chemical Company

2 - KRONOS 1000 TiO₂, KRONOS, Inc.

Referring to TABLE 3A and comparing the results of H-4 to H-1, it is evident that heating to 930 C with purer TiO₂ has a significant effect on the GEB value for the inventive pigment while offering comparable opacity (scatter coefficients) at 457 nm and 577 nm. However, in either case, H-4 and H-1 offer significant advantages for both GEB values and for 457 nm and 577 nm scatter coefficients compared with the C-1 clay pigment.

TABLE 3B

Property	C-2	H-2	H-5
Heat Treatment	1090 C	1090 C	1090 C
Components (wt.%): Clay TiO ₂	100% —	90% 10% ¹	90% 10% ²
Components Mixed before Heat Treatment	Single Component N/A	YES	YES
Components Mixed After Heat Treatment	Single Component N/A	NO	NO
GEB	92.7	81.5	88.3
Scatter Coefficient, 457nm (m ² /g)	0.296	0.368	0.395
Scatter Coefficient, 577nm (m ² /g)	0.256	0.328	0.307
Particle Size (% < 2 μ)	89.1	87.4	90.5

Notes: 1 - RPS VANTANGE TiO₂, DuPont Chemical Company
2 - KRONOS 1000 TiO₂, KRONOS, Inc.

Referring to TABLE 3B and comparing the results of H-5 to H-2, it is evident that heating to 1090 C with purer TiO₂ has a significant effect on the GEB value for the inventive pigment while maintaining comparable opacity (scatter coefficients at 457 nm and 577 nm). However, in either case, H-5 and H-4 offer significant advantages for opacity (scatter coefficients) but suffer in terms of GEB brightness compared with the C-2 clay pigment. However, as shown in Example 4, the lower GEB values for inventive pigments surprisingly did not have an ill effect on the coated sheet properties compared to commercially available clay pigments of substantially higher brightness.

Example 4

The example demonstrates the coated sheet properties of this invention and compares them to conventional clay-based pigments. Four (4) comparative coated sheets were prepared from three (3) pigments and a base coating hydrous clay have the following properties:

TABLE 4

Property	Hydrous Clay Miracclipse PG ¹	Luminex ²	C-1	H-1
Heat Treatment	None	1090	1090	930
Components (wt.%): Clay	100%	100%	100%	90%
TiO ₂	--	--	--	10%
Components Mixed before Heat Treatment	Single Component N/A	--	--	Yes
Components Mixed After Heat Treatment	Single Component N/A	--	--	No
GEB	90.3	96.8	92.7	82.6
Scatter Coefficient, 457nm (m ² /g)	0.116	0.290	0.296	0.381
Scatter Coefficient, 577nm (m ² /g)	0.099	0.266	0.256	0.338
Particle Size (% < 2 μ)	88	81.7	89.1	88.7

Notes: 1- Commercially available hydrous clay pigment available from Engelhard Corporation.

2- Commercially available high brightness calcined clay pigment available from Engelhard Corporation.

Using the above pigments, the four (4) coated sheets were prepared containing the following compositions and properties:

TABLE 5

<u>Component/Property</u>	<u>Coating 1</u>	<u>Coating 2</u>	<u>Coating 3</u>	<u>Coating 4</u>
MIRACLIPSE PG	80	80	85	80
LUMINEX	15	--	--	--
C-1	--	15	10	--
H-1	--	--	--	15
Latex PP 730 NA	5	5	5	5
Latex FC 1060 NA	14	14	14	14
FINN FIX 10	0.825	0.625	0.750	0.700
Coat Weight (lb./3300 ft ²)	5.1	5.0	4.9	5.0
Sheet Gloss (75°)	54	67.7	55	51
ISO BRIGHTNESS (%)	67.6	67.5	67.2	68.0
TAPPI BRIGHTNESS (%)	68.6	68.8	68.5	69.3
TAPPI OPACITY (%)	91.9	92.0	91.9	92.5
HUNTER				
L	83.7	83.8	83.6	84.4
a	0.48	0.49	0.50	0.35
b	2.71	2.64	2.69	2.90
Print Gloss -75° @ 14. o.d.	60	60	62	59
Parker Print Surf 10 Kg/cm	1.14	1.15	1.16	1.17
IGT Dry Pick	5	5	5	4
K & N %	22	22	21	21
Notes: Calendaring Conditions: PLI = 653; temp (°F) = 150; Speed (ft/min) = 37; passes = 2.				

As can be seen in TABLES 4 and 5, it is quite unexpected and unique that Coating 4, which contains the inventive pigment H-1 of this invention records higher ISO and TAPPI sheet brightness and higher TAPPI sheet opacity than Coatings 1, 2, and 3 despite the fact that pigment H-1 used in Coating 4 has a lower GEB value (GEB = 82.6) than the pigments used in Coating 1 (MIRACLIPSE PG, GEB = 90.3), Coating 2 (LUMINEX, GEB = 96.8), or Coating 3 (C-1, GEB = 92.7).

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The principles, preferred embodiments, and modes of operating of this invention have been described in the foregoing specification. However, the invention which is intended to be protected herein is not to be construed as limited to the particular forms disclosed, since they are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

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Claims

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What is claimed is:

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1. A paper filling or paper coating pigment derived from heating a hydrous clay with a metal oxide and/or a metal oxide precursor, the metal being selected from the group consisting of transition metals and post-transition metals and their combinations, said heating being applied to an extent sufficient to aggregate the metal oxide and/or metal oxide precursor with the clay.

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2. The pigment of claim 1, wherein the clay is a kaolin clay.

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3. The pigment of claim 2, wherein the heating does not exceed a temperature of 1200°C.

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4. The pigment of claim 3, wherein the heating is conducted in the temperature range of 400 to 800°C.

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5. The pigment of claim 3, wherein the heating is conducted in the temperature range of 800 to 1100°C.

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6. The pigment of claim 3, wherein the metal oxide is titania, zinc oxide, stannous oxide, or stannic oxide and the metal oxide precursor is titanyl chloride or titanyl sulfate.

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7. The pigment of claim 6, wherein the titania comprises from 0.5 to 50 percent by weight of the pigment.

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8. The pigment of claim 7, wherein the hydrous clay has a particle size distribution in the range of about 75 to 100 percent by weight finer than 1 micrometer.

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9. The pigment of claim 8, wherein the hydrous clay has a particle size distribution in the range of about 70 to 90 percent by weight finer than 0.5 micrometer.

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10. The pigment of claim 9, wherein the metal oxide is titania.

11. The pigment of claim 10, wherein the metal oxide precursor is titanyl chloride or sulfate.

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12. The pigment of claim 3, wherein the metal oxide or metal oxide precursor comprises from 5 to 20 percent by weight of the pigment.

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13. The pigment of claim 12, wherein the hydrous clay has a particle size distribution of about 85 to 95 percent by weight finer than 1 micrometer with approximately 70 to 80 percent by weight of the particles finer than 0.5 micrometer.

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14. A method for making a paper filling or paper coating pigment of improved opacity comprising the steps of:

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- (a) providing a hydrous clay;
- (b) mixing with the hydrous clay a transition metal or a post-transition metal oxide, their precursors, or combinations thereof;
- (c) heating the composition of step (b) to an extent sufficient to aggregate the metal oxide and/or metal oxide precursor with the clay.

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15. The method of claim 14, wherein the hydrous clay is a kaolin clay.

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16. The method of claim 15, wherein the kaolin clay has a particle size distribution of about 75 to 100 percent by weight finer than 1 micrometers.

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17. The method of claim 14, wherein the metal oxide and/or the metal oxide precursor comprises from 0.5 to 50 percent by weight of the pigment.

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18. The method of claim 17, wherein the metal oxide is titania, zinc oxide, stannous oxide, or stannic oxide and the metal oxide precursor is titanyl chloride or titanyl sulfate.

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19. The method of claim 18, wherein the clay has a particle size distribution of about 85 to 95 percent by weight finer than 1 micrometer with approximately 70 to 80 percent by weight of the particles finer than 0.5 micrometers.

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20. The method of claim 19, wherein the metal oxide is titania and the metal oxide precursor is titanyl chloride or sulfate.

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21. A paper comprising the pigment of claim 1.

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22. A paint pigment derived from heating a hydrous clay with a metal oxide and/or a metal oxide precursor, the metal being selected from the group consisting of transition metals and post-transition metals and their combinations, said heating being applied to an extent sufficient to aggregate the metal oxide and/or metal oxide precursor with the clay.

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Internal Application No.

A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Name and mailing address of the ISA European Patent Office, P.B. 5618 Petrusdijk 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3018	Authorized officer Nestby, K
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INTERNATIONAL SEARCH REPORT

Int. Appl. No.

PCT/US 99/28235

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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